

- Final Technical Report -

Infrared Probes of Metal Cluster Structure and Bonding

For the Period January 1, 2003 to December 31, 2005

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Michael A. Duncan

**Department of Chemistry
University of Georgia
Athens, GA 30602**

maduncan@arches.uga.edu
www.arches.uga.edu/~maduncan

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OBJECTIVES

The goal of this research program is to investigate the structure and bonding in stable metal-containing clusters which may be useful as precursors for "cluster-assembled materials." Nanoparticles containing metals may provide new catalysts with enhanced selectivity or media for solar energy cells of the future. New oxide nanoparticles may provide synthetic routes to improved ceramic materials, while networks of nanoparticles are expected to have unusual optical and electronic properties. In each of these cases, the enabling technology is the controlled synthesis of desired nanoparticles with favorable composition and stability. Our research project has explored new ways to make nanoparticles with new compositions and we have performed various experiments with which to characterize their properties. In this work, metal-containing clusters in the size range from a few up to several hundred atoms are prepared in the gas phase via laser vaporization of solid targets. We focus on metal carbide and oxide species, as well as metal-silicon clusters. Additionally, we investigate novel organometallics, in which metals bind to the surface of fullerenes or polycyclic aromatic systems. We use laser spectroscopy and mass spectrometry to measure the properties of these clusters, and comparisons are made to the predictions of theory to enhance the understanding of metal bonding interactions. Prospects are evaluated for macroscopic synthesis of cluster materials and synthesis experiments employing ligand-coating strategies have been initiated using a newly constructed "laser ablation flowtube reactor."

STATUS OF EFFORT

Gas phase experiments using laser photodissociation and laser spectroscopy were conducted on various metal-containing clusters using pulsed molecular beam machines coupled with time-of-flight mass spectrometers. These experiments explored the new kinds of nanocluster materials that can be produced and investigated their structures and stabilities. Synthesis experiments that isolate ligand-coated nanoclusters in solution were conducted using a new laser ablation flowtube reactor. Graduate and undergraduate

students were trained in various aspects of physical and inorganic chemistry as they apply to the gas phase synthesis and characterization of unusual nanocluster molecules.

ACCOMPLISHMENTS/NEW FINDINGS

Research in this project over the last three years has focused on three main areas: 1) photodissociation studies of metal oxide, carbide and silicide clusters; 2) production and characterization of new organometallic clusters and 3) the development of new technology (laser vaporization flowtube reactor) for the production and isolation of ligand-coated nanoclusters. Significant progress has been made in all three areas.

Metal Oxide Clusters

Over the last several years, our research group has investigated many examples of transition metal carbide and oxide clusters that are produced in molecular beams and studied with mass spectrometry and laser spectroscopy. Transition metal carbides have been a continuing area of study, and we have also investigated main group metal oxides in the past (magnesium oxide, aluminum oxide, etc.). In the last three years, we have turned the focus toward transition metal oxide clusters, and this is the area of our greatest progress. We have made various examples of clusters of the form $M_nO_m^+$ for transition metals (V, Nb, Ta, Fe, Cr), and have studied the bonding patterns in these systems with mass spectrometry and mass-selected laser photodissociation.

In the vanadium, niobium and tantalum oxides we saw common patterns in both the mass spectra and in the photodissociation. The oxides that grow from the cluster source do not represent random stoichiometries. Instead, a range of $M_nO_m^+$ species are produced where $m=2n+x$, and $x=2-4$. At each metal atom increment n , there are 4-5 mass peaks representing different values of m , i.e. there are several prominent oxide stoichiometries and not just one or two "magic number" clusters. The most common bulk stoichiometries for these metals is MO_2 or M_2O_3 , and the structures of the bulk oxides

have networks of alternating M-O-M-O- bonding. Therefore, the cluster stoichiometries suggest that similar networks of bonding form, but with excess oxygen atoms attached to the exterior of the cluster. Similar trends, but with different stoichiometries, are found for the iron and chromium oxide clusters studied more recently (see Figure 1).

Mass-selected laser photodissociation experiments reveal the patterns in cluster growth. These patterns are almost identical for the V, Nb and Ta oxide clusters. In each case, if we chose and excite clusters with excess oxygen, they fragment by elimination of oxygen only (sometimes atoms, sometimes O₂). As we proceed to smaller clusters with the same number of metal atoms but fewer oxygen atoms, we find a stable "core cluster" that does not eliminate more oxygen. Instead, this cluster size is difficult to dissociate at all, and when it does fragment it eliminates metal-containing oxide species, in a process analogous to fission. Additionally, patterns are apparent in the fission of core clusters. The same clusters identified as core species in oxygen stripping experiments are also produced as fragments when larger core clusters dissociate. For example, oxygen stripping identifies MO₂⁺, M₂O₄⁺, M₃O₇⁺, M₄O₉⁺, M₅O₁₂⁺ and M₇O₁₇⁺ species as the core oxides at each of these metal sizes; dissociation of M₇O₁₇⁺ produces M₄O₉⁺, M₃O₇⁺, etc. as fragments. The stable core oxides at each metal increment are the same for V, Nb and Ta. Significantly, these core oxide are not the most abundant species in the initial mass spectrum, and they were not identified by earlier experiments on the photoionization of the neutral clusters.

Chromium oxide clusters exhibit patterns similar to clusters in the vanadium group. However, there is an indication for a magic number at the Cr₄O₁₀⁺ cluster. This cluster is more abundant in the initial mass spectrum produced by the cluster source (Figure 1), and it is also prominent as a fragment from several larger clusters (Figure 2). On the other hand, iron oxides have stoichiometries and fragmentation patterns that are quite different. These clusters grow with excess oxygen beyond the 1:1 stoichiometry, except at small sizes where the Fe₂O₂⁺ and Fe₃O₃⁺ species are prominent (Figure 1). The Fe₃O₃⁺ cluster has been suggested by Khanna and Jena to have a six-membered ring structure. However, fragmentation strongly prefers the formation of species with 1:1 M:O ratios (Figure 2).

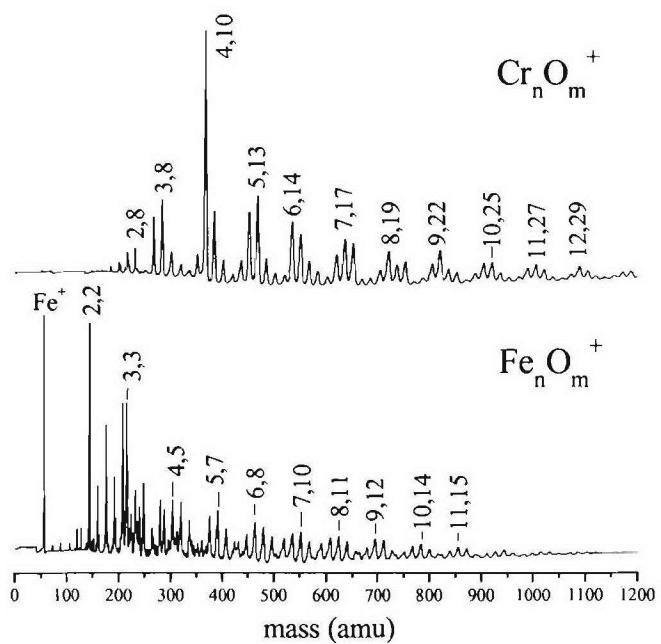


Figure 1. The mass spectrum of chromium and iron oxide cluster cations.

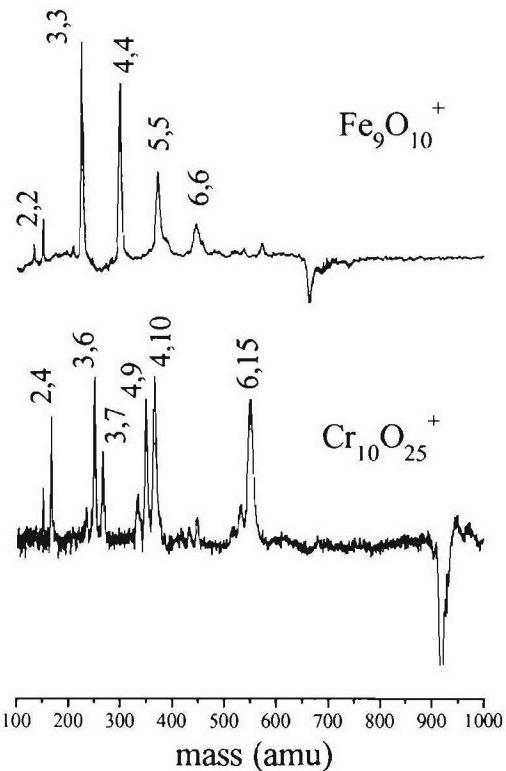


Figure 2. The photodissociation of mass-selected $\text{Fe}_9 \text{O}_{10}^+$ and $\text{Cr}_{10} \text{O}_{25}^+$.

Related to the work on metal oxide clusters, we have initiated a study of oxide and sulfide clusters of the aluminum group metals (Al, Ga, In). This work has been done by two undergraduate students, Ben Ham and Chantelle Anfuso. Magic number stoichiometries are found for these species that are essentially the same for all three metals. These stoichiometries are not the same as those for the corresponding oxide clusters, and can be explained with Wade's Rules for counting the valence electrons in bonding molecular orbitals. As an aside, Mr. Ham was just announced as one of this year's recipients for the prestigious Goldwater Scholars Award.

Metal Carbide and Silicide Clusters

As noted above, we have worked extensively in the past on transition metal carbides of metals like titanium and vanadium, and these species form magic number clusters in the gas phase. Less is known about noble metal carbides, partly because they are harder to make. In the case of early transition metals, we used laser vaporization of the metal sample with a gas flow containing a few percent of methane. Reaction of metal with methane in the hot plasma conditions produced the carbide clusters. However, this method does not work for the noble metals because they are much less reactive. To produce noble metal carbides, we coated a graphite rod with thin films of copper, silver or gold. Laser vaporization of these composite samples produced the desired metal carbide clusters. We were interested to see if these systems would have metal-centered structures, or structures composed of a pure carbon cluster with metal adsorbed on its surface. Our photodissociation patterns for copper and silver clusters found mostly elimination of metal, consistent with the latter scenario. However, gold clusters gave evidence for stable carbides with some metal-centered structures.

Similar behavior was found for noble metal-silicon clusters. Previous work on metal silicon clusters had suggested only metal-centered structures. However, in the case of copper and silver-silicon species, we found clear evidence for the efficient elimination of

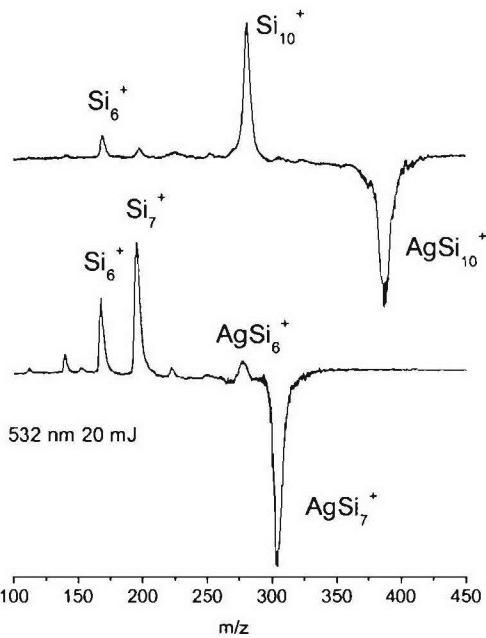


Figure 3. The photodissociation mass spectrum of mass-selected AgSi_{10}^+ and AgSi_7^+ , where the major fragments are Si_{10}^+ and Si_7^+ . These patterns indicate that the metal atoms are bound externally.

metal, consistent with silicon clusters having surface-adsorbed metal (see Figure 3). Photodissociation experiments on chromium-silicon clusters, however, produce more metal-silicon and pure silicon fragments, consistent with the proposed internal-metal structures (see Figure 4).

We also studied small silicon carbide clusters with mass-selected laser photodissociation. We identified Si_3C^+ and Si_7C^+ as stable cations and Si_2C and Si_3C as the most stable neutral species.

Synthesis of Macroscopic Cluster Materials

Macroscopic amounts of cluster-based materials have been isolated in the past for species such as the fullerenes, metal-encapsulated fullerenes, semiconductor quantum dots, noble metal clusters and a few examples of metal oxide nanoparticles. Except for the fullerenes, these species are stabilized for isolation because they have ligand or surfactant coatings. However, there is no general method for the production of

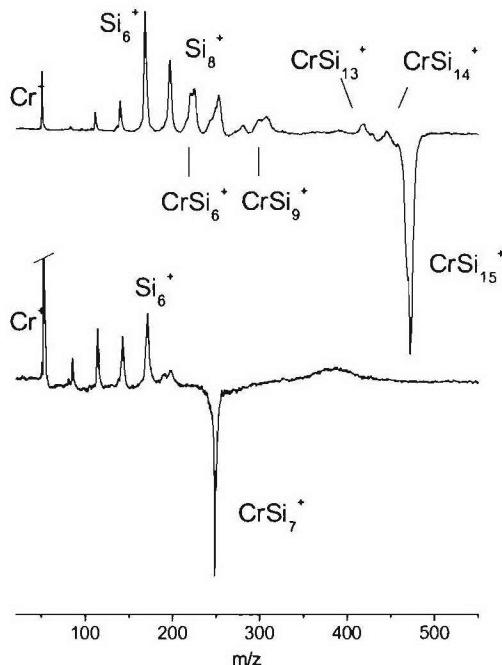


Figure 3. The photodissociation mass spectrum of mass-selected CrSi_{15}^+ and CrSi_7^+ . These patterns indicate that the metal atoms are bound externally for the CrSi_7^+ species, but probably internally for the CrSi_{15}^+ species.

transition metal clusters or those containing transition metal oxides and carbides in isolated form. Our research program has studied many of these latter cluster systems in the gas phase, and we have recently set out to obtain them in macroscopic quantities. To do this, we have developed a laser ablation flowtube reactor (LAFR) that produces gas phase clusters via the same laser vaporization method that we use in the gas phase. The laser repetition rate is higher to allow greater duty cycle for the method. Clusters are produced in a flowing gas mixture where they are cooled as they grow and then stabilized against reactions and further growth by coating them with ligands. The LAFR device has been in operation in our group for about three years, and we have recently found the right combination of conditions needed to isolate a number of interesting cluster species. For example, we have focused on the same vanadium oxide clusters that were shown to have high stability in our molecular beam experiments. Figure 5 shows the mass spectrum of the *solution* produced when vanadium oxide clusters are produced in the gas phase and coated with THF ligands and trapped in excess THF

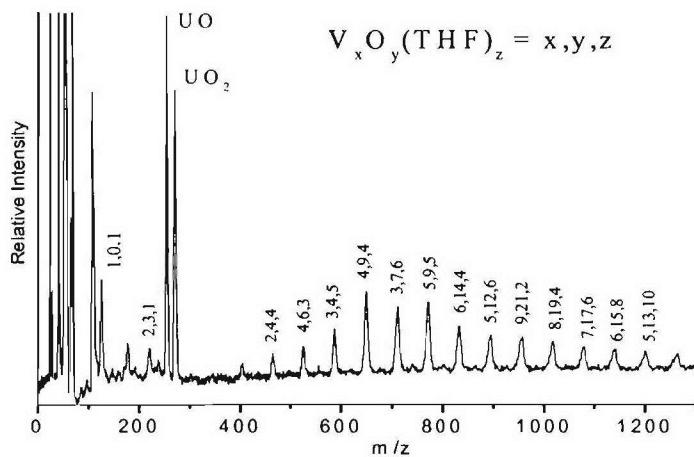


Figure 5. The mass spectrum from the solution isolated after vanadium oxide clusters are produced and coated with THF ligands. UO and UO_2 are present as impurities in the mass spectrometer from a previous experiment.



Figure 6. The laser vaporization flow-tube apparatus with on-line mass spectrometer system.

solvent. As indicated, a variety of clusters are detected in this mass spectrum that contain vanadium, oxygen and THF. Remarkably, many of these masses have exactly the same oxide stoichiometries as the clusters that we identified to be stable in the gas phase (e.g., V₃O₇, V₇O₁₇, etc.). For example, one of the masses detected is the species V₃O₇(THF)₆. This is a particularly exciting result. To our knowledge, this is the first time that magic number clusters from gas phase experiments have been isolated as ligand-coated species. Further work is underway to try to isolate the corresponding niobium and tantalum analogues of these clusters.

Preliminary attempts were conducted for the production of other ligand-coated clusters, and some promising results were obtained. However, we found that it is difficult to adjust the operating conditions of the LAFR instrument without some diagnostics on the source and how various conditions affect its output. We therefore wrote a proposal to the DURIP instrumentation program for the addition of an on-line mass spectrometer system to the LVFR device. This request was funded last year, and we have constructed this device this past year. The full apparatus, including the flow tube and the online mass spectrometer is now assembled (Figure 6), and initial testing of this instrument is in progress. We expect that this new methodology will allow the isolation of many ligand-coated nanocluster systems as our work continues.

Metal Complexes with Polycyclic Aromatic Hydrocarbons (PAH's)

Previous experiments in our lab demonstrated how the laser vaporization process could be employed with organic film-coated metal rods to make cluster networks and sandwiches composed of metal-fullerenes and metal-PAH species. In recent work we have extended these studies to make a wider variety of metal-PAH complexes and to make metal oxide and chloride clusters supported on PAH surfaces. Additional work has employed the bowl-shaped molecule corannulene for similar studies. In work related to this, we produced the first uranium-benzene and uranium oxide-benzene cluster ions and studied these with photodissociation. Photodissociation of the U⁺(bz)_{1,2} species leads to fragmentation of the benzene and the production of metal-hydrocarbon fragments. On the

other hand, fragmentation of $\text{UO}^+(\text{bz})_{1,2}$ or $\text{UO}_2^+(\text{bz})_{1,2}$ gave simple elimination of intact benzene. The oxide are therefore concluded to be less reactive than the bare cation of uranium.

Mass Spectrometry Studies of Nanotube Reactions

We have initiated a collaboration with Prof. Thomas Manning at Valdosta State University (an undergraduate institution). Professor Manning studies the degradation products of the reactions of fullerenes and carbon nanotubes with ozone or nitric acid. Our lab provides the mass spectrometry analysis for samples before and after these reactions. The work takes advantage of the unique laser desorption mass spectrometer that we have developed as part of our cluster synthesis laboratory, and it established a collaboration that involves additional undergraduate students in this research.

PERSONNEL SUPPORTED BY AND/OR ASSOCIATED WITH THIS PROJECT

Faculty:

Professor Michael A. Duncan (one month summer salary each year)

Graduate Students:

| | |
|----------------------|---------------|
| Todd Jaeger | Ph.D. program |
| Timothy Ayers | Ph.D. program |
| Jared Jaeger | Ph.D. program |
| Karen Sinclair Molek | Ph.D. program |
| Brian Ticknor | Ph.D. program |

Postdoctoral Fellows:

none

Undergraduate Students

Ben Ham, UGA Undergrad.
Chantelle Anfuso, UGA Undergrad.

PUBLICATIONS RESULTING FROM THIS PROJECT

1. G. Gregoire, N. Brinkman, H.F. Schaefer and M.A. Duncan, "Infrared Photodissociation Spectroscopy of Mg⁺-(CO₂)_n and Mg⁺-(CO₂)_nAr_m Complexes," *J. Phys. Chem. A* **107**, 218 (2003).
2. D. van Heijnsbergen, K. Demyk, M.A. Duncan, G. Meijer and G. von Helden, "Structure Determination of Aluminum Oxide Clusters," *Phys. Chem. Chem. Phys.* **5**, 2515 (2003).
3. T.M. Ayers, J.L. Fye, Q. Li and M.A. Duncan, "Synthesis and Isolation of Titanium Metal Cluster Complexes and Ligand-coated Nanoparticles with a Laser Vaporization Flowtube Reactor," *J. Clus. Sci.* **14**, 97 (2003).
4. T.M. Ayers, B.C. Westlake and M.A. Duncan, "Laser Plasma Production of Metal and Metal-Compound Complexes with PAH's," *J. Phys. Chem. A* **108**, 9805 (2004).
5. E.D. Pillai, K.S. Molek and M.A. Duncan, "Growth and Photodissociation of U⁺(C₆H₆)_n (n=1-3) and UO_m⁺(C₆H₆) (m=1,2) Complexes," *Chem. Phys. Lett.* **405**, 247 (2005).

6. B.W. Ticknor and M.A. Duncan, "Photodissociation of size-selected silicon carbide cluster cations," *Chem. Phys. Lett.* **405**, 214 (2005).
7. K. Olsen, L. Hardin, J. McGovern, T. Manning, D. Phillips, T.M. Ayers and M.A. Duncan, "Nanoresistors and Single-Walled carbon Nanotubes: Using an Ohmmeter to Test for Hybridization Shifts," *Chem. Educator* **10/4**, 260 (2005).
8. T.J. Manning, K. Olsen, L. Hardin, J. Purcell, T.M. Ayers and M.A. Duncan, "Bulk degradation of carbon nanotubes by ozone and nitric acid, *Ozone Sci. & Eng.*, in press.
9. T.J. Manning, K. Olsen, L. Hardin, J. Purcell, T.M. Ayers and M.A. Duncan, "Extensive ozonation of C₆₀: Degradation or polymerization?," *Ozone Sci. & Eng.*, in press.
10. T. Ayers, B.C. Westlake, D.V. Preda L.T. Scott and M.A. Duncan, "Laser Plasma Production of Metal-Corannulene Ion-Molecule Complexes," *Organometallics* **24**, 4573 (2005).
11. K.S. Molek, T.D. Jaeger and M.A. Duncan, "Photodissociation of Vanadium, Niobium and Tantalum Oxide Cluster Cations," *J. Chem. Phys.* **123**, 144313 (2005).
12. T. M. Ayers, P. B. Ham III, M. A. Duncan, "Production of Inorganic Nanoclusters Using Laser Desorption Time-of-Flight Mass Spectrometry," *J. Chem. Ed.*, submitted.
13. T.M. Ayers, B.C. Westlake, M.A. Duncan, "Synthesis of Ligand-Coated Vanadium Oxide Nanoclusters with a Laser Vaporization Flowtube Reactor," *J. Phys. Chem. B*, to be submitted.

INTERACTIONS/TRANSITIONS

a) PRESENTATIONS

Lectures Presented by the PI on this Research

1. "Vibrational Spectroscopy of Metal Carbide and Oxide Nanoclusters," *Plenary Lecture, 21st Century COE Keio LCC Conference on the Nanoscale World*, Keio University, Yokohama, Japan, February 2003.
2. "Infrared Probes of Chemistry on Size-Selected Metal Clusters," *National Meeting of the American Chemical Society, Symposium on Nanocluster Catalysis*, New York, September 2003.

3. "Metal Carbide Nanoclusters and Nanocrystals: Discovering Stardust in the Laboratory," *Natural Science Colloquium*, Valdosta State University, September 2003.
4. "Metal Carbide Nanoclusters and Nanocrystals: Discovering Stardust in the Laboratory," *Chemistry Colloquium*, College of William and Mary, November 2003.
5. "Metal Carbide Nanoclusters and Nanocrystals: Discovering Stardust in the Laboratory," *J.A. Southern Lecture*, Department of Chemistry, Furman University, April 2004.
6. "Photodissociation of Cation-Molecular Complexes, Carbon Clusters and Silicon Carbide Clusters," *Departmental Seminar*, Institute of Physical Chemistry, University of Basel, Switzerland, March 2005.
7. "Metal Carbide and Oxide Clusters: From Nanoscience to Astrophysics," *Carolina-Piedmont Section of the American Chemical Society*, Charles H. Stone Award Lecture, Davidson College, November 2005.
8. "Photodissociation and Infrared Spectroscopy of Mass-Selected Metal-Containing Clusters," *Physical Chemistry Seminar*, Penn State University, December 2005.
9. *Frontiers in Spectroscopy Lecture Series*: 2) "Development of the Laser Vaporization cluster Source," Department of Chemistry, Ohio State University, February, 2006.
10. "Infrared Photodissociation and Spectroscopy of Gas Phase Metal Clusters," *Chemistry Departmental Seminar*, Florida State University, February 2006.

Contributed Presentations by the PI and Students

1. T.M. Ayers, J.L. Fye, Q. Li and M.A. Duncan, "Synthesis and Isolation of Titanium Metal Cluster Complexes and Ligand-coated Nanoparticles with a Laser Vaporization Flowtube Reactor," *International Symposium on Clusters and Nanoassemblies*, Richmond, VA, November 2003.
2. K. Olsen, J. Smith, J. Purcell, T. Manning, K. Riddle, M. Duncan, T. Ayers, D. Phillips, "Bucky-acids and ten forms of carbon: Converting new science into general chemistry labs," *55th Southeast Regional Meeting of the American Chemical Society*, Atlanta, GA, November 2003.
3. M.A. Duncan, "Metal Compound Nanoclusters: Gas Phase Studies and Isolation Strategies," *AFOSR Molecular Dynamics Program Contractor's Meeting*, Newport, RI, May 2004.

4. T.M. Ayers and M.A. Duncan, "Synthesis and Isolation of Ligand-Coated Metal Clusters in a Laser Vaporization Flowtube Reactor," University of Bristol, UK, June 2004.
5. B. Ham, T.D. Ayers and M.A. Duncan, "Laser ablation to produce new Al, Ga and In sulfide clusters," University of Georgia, Council on Undergraduate Research Symposium, April 2005 (poster).
6. B. Ham, T.D. Ayers and M.A. Duncan, "Laser ablation to produce new Al, Ga and In sulfide clusters," Southeast Regional Meeting of the American Chemical Society's Student Affiliates, Mississippi State University, April 2005.
7. M.A. Duncan, "Gas phase studies and isolation strategies for transition metal oxide clusters," *AFOSR Molecular Dynamics Program Review*, Monterey, CA, May 2005 (poster).
8. B. Ticknor, L. Belau, M. Ahmed, S.R. Leone and M.A. Duncan, "Vacuum UV threshold photoionization of carbon clusters at the Advanced Light Source," Gordon Research Conference on *Molecular and Ionic Clusters*, Ventura, CA, February 2006 (poster).

b) CONSULTATIVE AND ADVISORY FUNCTIONS

none

c) TRANSITIONS

Oral Presentation at Contractor's Meeting: M.A. Duncan, "Metal Compound Nanoclusters: Gas Phase Studies and Isolation Strategies," *AFOSR Molecular Dynamics Program Contractor's Meeting*, Newport, RI, May 2004.

Poster presentation at Contractor's Meeting: M.A. Duncan, "Photodissociation of transition metal oxide clusters," *AFOSR Molecular Dynamics Program Contractor's Meeting*, Monterey, CA, May 2005.

NEW DISCOVERIES, INVENTIONS OR PATENT DISCLOSURES

none

PI HONORS/AWARDS

Elected Fellow, American Association for the Advancement of Science (AAAS), 2004.
Received Charles H. Stone Award, Carolina-Piedmont Section, American Chemical Society, October 2005 (for Chemist of the Year in the Southeast).

REPORT DOCUMENTATION PAGE

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| 14. ABSTRACT Molecular beam experiments employing laser vaporization, time-of-flight mass spectrometry and laser photodissociation were employed to study a variety of metal compounds nanoclusters to evaluate their potential for new materials. Mixed atomic clusters of copper, silver and gold with carbon or silicon were studied as well as several transition metal oxide clusters. New laser techniques were developed and employed to make metal and metal oxide complexes with polycyclic aromatic hydrocarbon species. In a combination of laser vaporization methods with inorganic synthetic methodology, ligand-coated metal and metal oxide clusters for the early transition metals titanium and vanadium were synthesized and collected in macroscopic amounts for the first time. These oxides are sub-nanometer in size, representing some of the smallest particles ever isolated. | | | | | | |
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